Pulverulent flame-retardant composition with low dust level, its use, and process for its preparation, and flame-retardant polymeric molding compositions

The present invention relates to a pulverulent flame-retardant composition with low dust level, composed of an organophosphorus flame-retardant component, and of at least one dust-reduction additive, to a process for preparing this pulverulent flame-retardant composition with low dust level, and also to polymeric molding compositions, and to moldings which comprise this pulverulent flame-retardant composition with low dust level.

Organophosphororus compounds are used as flame retardants for thermoplastics such as polyamides or polyesters.

In these application sectors, the processing of the organophosphorus flame-retardant component is often made difficult by a tendency toward dusting.

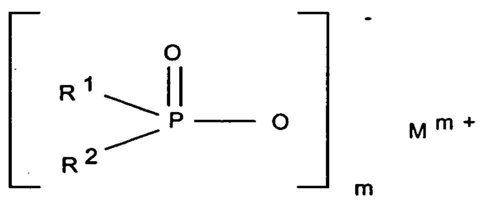
The tendency toward dusting is a disadvantage during transfer of the solid, causes escape of the substance into the environment, and causes contamination of industrial plants, and in extreme cases can cause dust explosions.

It was therefore an object to reduce the tendency of flame-retardant compositions toward dusting, while retaining, or improving, the flowability of these flame-retardant compositions.

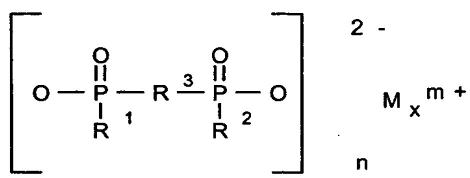
The object is achieved by way of a pulverulent flame-retardant composition with low dust level, composed of an organophosphorus flame-retardant component, and of at least one dust-reduction additive.

Surprisingly, it has now been found that addition of a dust-reduction additive is effective in reducing the tendency toward dusting, and can at the same time give retention of, or improvement in, flowability.

The organophosphorus flame-retardant component preferably comprises a phosphinic salt of the formula (I) and/or a diphosphinic salt of the formula (II) and/or polymers of these (component A),



(I)



(II)

where

R^1 and R^2 are identical or different and are C_1-C_6-alkyl, linear or branched, and/or aryl;

R^3 is C_1-C_{10}-alkylene, linear or branched, C_6-C_{10}-arylene, -alkylarylene, or -arylalkylene;

M is Mg, Ca, Al, Sb, Sn, Ge, Ti, Zn, Fe, Zr, Ce, Bi, Sr, Mn, Li, Na, K, and/or a protonated nitrogen base;

m is from 1 to 4;

n is from 1 to 4;

x is from 1 to 4.

M is preferably calcium, aluminum, or zinc.

Protonated nitrogen bases are preferably the protonated bases of ammonia, melamine, or triethanolamine, in particular NH_4^+.

Preferred meanings of R^1 and R^2, identical or different, are C_1-C_6-alkyl, linear or branched, and/or phenyl.

Particularly preferred meanings of R^1 and R^2, identical or different, are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, and/or phenyl.

Preferred meanings of R^3 are methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, n-pentylene, n-octylene, or n-dodecylene.

Other preferred meanings of R^3 are phenylene or naphthylene.

Other preferred meanings of R^3 are methylphenylene, ethylphenylene, tert-butylphenylene, methylnaphthylene, ethylnaphthylene, or tert-butylnaphthylene.

Other preferred meanings of R^3 are phenylmethylene, phenylethylene, phenylpropylene, or phenylbutylene.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component also preferably comprise(s) melamine phosphate, dimelamine phosphate, melamine pyrophosphate, melamine polyphosphates, melam polyphosphates, melem polyphosphates, and/or melon polyphosphates.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component also preferably comprise(s) melamine condensation products, such as melam, melem, and/or melon.

Suitable substances are condensation products of melamine or reaction products of melamine with phosphoric acid, and reaction products of condensation products of melamine with phosphoric acid, and also mixtures of the products mentioned. Examples of condensation products of melamine are melem, melam, or melon, and compounds of this type but with a higher condensation level, and also mixtures of the same. One way of preparing these condensation products uses a process described in WO-A-96/16948.

The reaction products with phosphoric acid are compounds resulting from reaction of melamine or of the condensed melamine compounds, such as melam, melem, or melon, etc., with phosphoric acid. Examples of these are melamine polyphosphate, melam polyphosphate, and melem polyphosphate, and mixed polysalts, e.g. as described in PCT/WO 98/39306. The compounds mentioned have been disclosed previously in the literature, and may also be prepared via processes other than the direct reaction with phosphoric acid. For example, melamine polyphosphate may be prepared by a method based on PCT/WO 98/45364, by reacting polyphosphoric acid and melamine, or by a method based on PCT/WO 98/08898 by condensation of melamine phosphate or melamine pyrophosphate.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component also preferably comprise(s) oligomeric esters of tris(hydroxyethyl) isocyanurate with aromatic polycarboxylic acids, benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine, melamine cyanurate, dicyandiamide, and/or guanidine.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component preferably comprise(s) nitrogen-containing phosphates of the formulae $(NH_4)_y H_{3-y} PO_4$ and, respectively, $(NH_4 PO_3)_z$, where y is from 1 to 3 and z is from 1 to 10 000.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component preferably comprise(s), as component B, a synthetic inorganic compound and/or a mineral product.

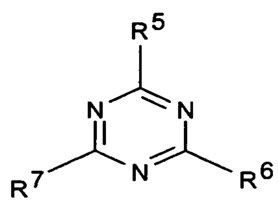
Component B is preferably an oxygen compound of silicon, or is magnesium compounds, is metal carbonates of metals of the second main group of the Periodic Table, is red phosphorus, is zinc compounds, or is aluminum compounds.

The oxygen compounds of silicon are particularly preferably salts and esters of orthosilicic acid and condensation products thereof, or are silicates, zeolites, and silicas, are glass powder, glass/ceramic powder, or ceramic powder; the magnesium compounds are magnesium hydroxide, hydrotalcites, magnesium carbonates, or

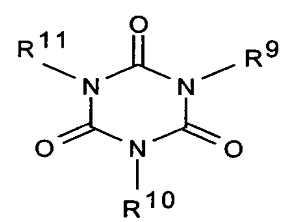
magnesium calcium carbonates; the zinc compounds are zinc oxide, zinc stannate, zinc hydroxystannate, zinc phosphate, zinc borate, or zinc sulfides; the aluminum compounds are aluminum hydroxide or aluminum phosphate.

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component preferably comprise(s) nitrogen compounds as further component C.

The nitrogen compounds are preferably those of the formulae (III) to (VIII) or mixtures thereof



(III)



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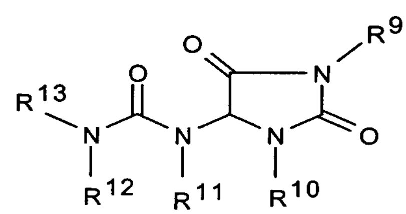

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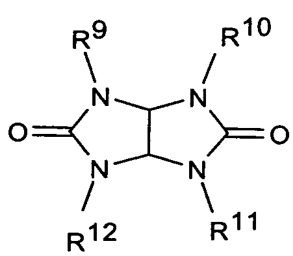

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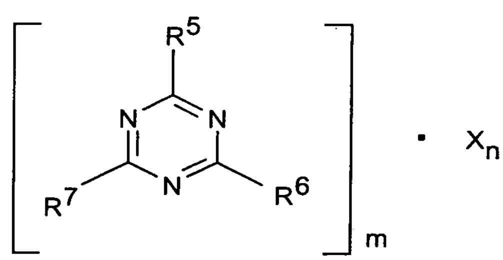

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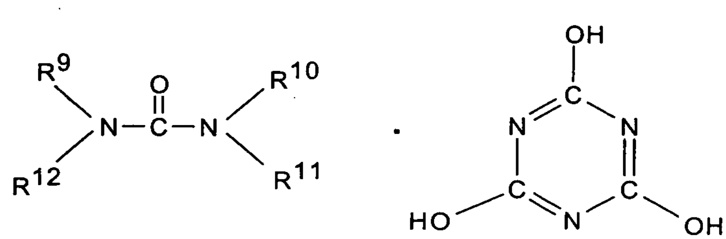

(VIII)

where

R^5 to R^7 are hydrogen, C_1-C_8-alkyl, or C_5-C_{16}-cycloalkyl or -alkylcycloalkyl, unsubstituted or substituted with a hydroxy function or with a C_1-C_4-hydroxyalkyl function, or are C_2-C_8-alkenyl, C_1-C_8-alkoxy, -acyl, or -acyloxy, are C_6-C_{12}-aryl or -arylalkyl, are $-OR^8$ or $-N(R^8)R^9$, or else are N-alicyclic systems or N-aromatic systems,

R^8 is hydrogen, C_1-C_8-alkyl, C_5-C_{16}-cycloalkyl or -alkylcycloalkyl, unsubstituted or substituted with a hydroxy function or with a C_1-C_4-hydroxyalkyl function, or is C_2-C_8-alkenyl, C_1-C_8-alkoxy, -acyl, or –acyloxy, or is C_6-C_{12}-aryl or -arylalkyl,

R^9 to R^{13} are the groups of R^8, or else $-O-R^8$,

m and n, independently of one another, are 1, 2, 3, or 4,

X is acids which can form adducts with triazine compounds (III).

The pulverulent flame-retardant composition with low dust level and/or the organophosphorus flame-retardant component preferably also comprise(s) carbodiimides.

The invention also includes synergistic combinations of the phosphinates mentioned with the abovementioned nitrogen-containing compounds, these being more effective than the phosphinates alone as flame retardants in very many polymers (DE-A-196 14 424, DE-A-197 34 437, and DE-A-197 37 727). The flame-retardant action of surface-modified phosphinates may be improved by combination with other flame retardants, preferably with nitrogen-containing synergists or with phosphorus/nitrogen flame retardants.

The preferred bulk density of the organophosphorus component is from 80 to 800 g/l, particularly preferably from 200 to 700 g/l.

Preferred dust-reduction additives are akylalkoxylates, among which preference is given to ethoxylated alcohols, preferably primary alcohols, preferably having from 8 to 22 carbon atoms, and preferably having from 1 to 80 EO units per mole of alcohol, the alcohol radical being linear or preferably methyl-branched at the 2-position, or comprising a mixture of linear and methyl-branched radicals, as is usually the case in oxo alcohol radicals. Examples of preferred ethoxylated alcohols are the C_{11} alcohols having 3, 5, 7, 8 or 11 EO units, (C_{12}-C_{15}) alcohols having 3, 6, 7, 8, 10 or 13 EO

units, (C_{14}-C_{15}) alcohols having 4, 7 or 8 EO units, (C_{16}-C_{18}) alcohols having 8, 11, 15, 20, 25, 50 or 80 EO units, and mixtures of same, e.g. the ®Genapol grades T80, T110, T150, T200, T250, T500, T800 from the company Clariant GmbH. The degrees of ethoxylation given are statistical averages which for a specific product may be an integer or a non-integer. In addition to these, use may also be made of fatty alcohol-EO/PO adducts.

Other preferred dust-reduction additives are paraffin oils and, respectively, mineral oils whose boiling points are above about 360°C, soft paraffin wax with a melting point of from about 38 to 60°C, fully refined paraffin waxes with melting points of from about 60 to 62°C, and chlorinated paraffin oil, with a chlorine content of 70%, and with a viscosity of 1 200 centipoise.

Other preferred dust-reduction additives are silicone oils whose molar masses are from 1 000 to 150 000 g/mol, and with viscosities of from 10 to 1 000 000 mPas. Examples are Wacker AK 35® silicone oil and AK 100® silicone oil (polydimethylsiloxanes), Wacker Z 30® silicone oil (octamethylcyclotetrasiloxane).

Preference is also given to halogen- (e.g. chlorine- and/or fluorine-)substituted silicones, or functionalized silicones, e.g. amino-, vinyl-, or allyl-functional silicones.

Methylphenylpolysiloxanes are also preferred.

Preference is also given to copolymeric siloxanes, e.g. of dimethylpolysiloxanes and polyalkylene ethers (e.g. grade SF 1066® from General Electric Co., USA, with a viscosity of 1 600 centipoise).

Other preferred dust-reduction additives are ethylene glycol, its oligomers and/or polymers, and their ethers. Other preferred dust-reduction additives are propylene glycol, its oligomers and/or polymers, and their ethers. Other preferred dust-reduction additives are butylene glycol, its oligomers and/or polymers, and their ethers.

Other preferred dust-reduction additives are castor oil, glycerol, di-2-ethylhexyl phthalate, and polyesters of phthalic acid.

Other preferred dust-reduction additives are aromatic and aliphatic esters of phosphoric acid, e.g. diphenyl cresyl phosphates, tricresyl phosphates, diphenyl 2-ethylhexyl phosphates, and tris-2-ethylhexyl phosphates, tris(chloroisopropyl) phosphate, triethyl phosphate, and the diethyl ester of N,N-dihydroxyethyl-aminomethanephosphonic acid.

Another preferred dust-reduction additive is Astacin Finish PUD® (BASF AG, Ludwigshafen, 40%, aqueous, a dispersion of an anionic polyester polyurethane in accordance with DE 2 645 779 C3).

Other preferred dust-reduction additives are waxes. These are naturally occurring or synthesized substances which at 20°C are solid and kneadable and above 40°C melt without decomposition and have low viscosity. Waxes generally convert to the molten, low-viscosity state at from 50 to 90°C, or in exceptional cases at up to about 200°C. A distinction is made between naturally occurring waxes, such as carnauba wax, chemically modified waxes, such as montan ester waxes, and synthetic waxes, such as polyethylene waxes.

Preferred montan waxes for polymer processing are internal and external lubricants for the processing of polyvinyl chloride, polyolefins, polyamide, polystyrene, linear polyesters, thermoplastic polyurethane, curable molding compositions, and other polymers. They are downstream products from the refining of crude montan wax, which is obtained by extracting brown coal. They are long-chain carboxylic acids having chain lengths of from C_{28} to C_{32}, or are their full or partial esters with ethylene glycol, glycerol, or butylene glycol, or are alkaline earth metal salts of partially hydrolyzed esters, e.g. Licowax E®, Licowax WE 4®, and Licowax OP®.

Preferred polyethylene waxes are suitable for the polymer sector (PVC, rubber, polyolefins), examples being Licowax PE 520®, Licowax PE 810®, Licowax PE 820®, Licowax PE 830®, Licowax PE 840®, Licomont CaV®, Licolub WE4®, Ceridust 5551®.

Particular preference is given to dispersed or micronized waxes, e.g. Agrocer® 09 (aqueous wax dispersion based on montan wax, comprises 23% of wax), or Ceridust 5551®, partially saponified ester wax of a montanic acid, micronized, particle size 9 µm, from the company Clariant GmbH.

The dust-reduction additive preferably comprises naturally occurring, chemically modified, and/or synthetic waxes, particularly preferably carnauba waxes and montan waxes.

Preferred dust-reduction additives are esters, amides, anhydrides, hydrates, and salts of saturated aliphatic mono-, di-, tri-, and polycarboxylic acids.

Other preferred dust reduction additives are C_1-C_{20}-(alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl) monocarboxylates, C_1-C_{20}-(alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl) dicarboxylates, C_1-C_{20}-(alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl) tricarboxylates, C_1-C_{20}-(alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl) oligocarboxylates, C_1-C_{20}-(alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl or aryl) polycarboxylates.

Other preferred dust-reduction additives are monoorganyl or diorganyl esters of a dicarboxylic acid; monoorganyl, diorganyl, or triorganyl esters of a tricarboxylic acid; monoorganyl, diorganyl, triorganyl, or oligoorganyl esters of an oligocarboxylic acid; monoorganyl, diorganyl, triorganyl, oligoorganyl, or polyorganyl esters of a polycarboxylic acid, or a mixture of these.

Other preferred dust-reduction additives are esters of phthalic acid, among which are monoorganyl esters of phthalic acid and bisorganyl esters of phthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl or aryl), preference being given to monoalkyl esters of phthalic acid and dialkyl esters of phthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. dimethyl phthalate, diethyl phthalate, dipropyl phthalate, diisopropyl phthalate, dibutyl phthalate, epoxidized di(2-ethylhexyl) phthalate, diisooctyl phthalate, dioctyl phthalate, diisononyl phthalate, n-octyl phthalate, n-decyl phthalate, diisodecyl phthalate, butyl benzyl phthalate, butyl cyclohexyl phthalate, dicapryl phthalate,

di(3,5,5-trimethylhexyl) phthalate, di(1-allyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate.

Other preferred dust-reduction additives are esters of isophthalic acid, among which are monoorganyl esters of isophthalic acid and bisorganyl esters of isophthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of isophthalic acid and dialkyl esters of isophthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. di(2-ethylhexyl) isophthalate.

Other preferred dust-reduction additives are esters of terephthalic acid, among which are monoorganyl esters of terephthalic acid and bisorganyl esters of terephthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of terephthalic acid and dialkyl esters of terephthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are esters of oxalic acid, esters of malonic acid (e.g. di(2,2,6,6-tetramethylpiperidin-4-yl) diethylmalonate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) dibutylmalonate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate), esters of succinic acid (e.g. di(2,2,6,6-tetramethylpiperidin-4-yl) succinate), and esters of glutaric acid (e.g. di(2,2,6,6-tetramethylpiperidin-4-yl) glutarate).

Other preferred dust-reduction additives are esters of adipic acid, among which are monoorganyl esters of adipic acid and bisorganyl esters of adipic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of adipic acid and dialkyl esters of adipic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. dimethyl adipate, diethyl adipate, di-n-propyl adipate, diisopropyl adipate, di-n-butyl adipate, diisobutyl adipate, di-tert-butyl adipate, di(n-octyl) adipate, di(2-ethylhexyl) adipate, diisodecyl adipate, n-octyl adipate, 2-ethylhexyl adipate, n-decyl adipate, isodecyl adipate, di(2,2,6,6-tetramethylpiperidin-4-yl) adipate.

Other preferred dust-reduction additives are esters of pimelic acid, suberic acid, esters of azelaic acid (e.g. dialkyl azelate, particularly di(2-ethylhexyl) azelate, and esters of 1,13-tridecanedicarboxylic acid (brassylic acid).

Other preferred dust-reduction additives are esters of sebacic acid, among which are monoorganyl esters of sebacic acid and diorganyl esters of sebacic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of sebacic acid and dialkyl esters of sebacic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. dialkyl sebacate, particularly di(2-ethylhexyl) sebacate, di(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, di(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, di(1,2,3,6-tetramethyl-2,6-diethyl-piperidin-4-yl) sebacate, di(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, di(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

Other preferred dust-reduction additives are esters of tetrahydrophthalic acid, among which are monoorganyl esters of tetrahydrophthalic acid and bisorganyl esters of tetrahydrophthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of tetrahydrophthalic acid and dialkyl esters of tetrahydrophthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. di(2-ethylhexyl) tetrahydrophthalate.

Other preferred dust-reduction additives are esters of tetrahydroisophthalic acid, among which are monoorganyl esters of tetrahydrophthalic acid and bisorganyl esters of tetrahydroisophthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of tetrahydroisophthalic acid and dialkyl esters of tetrahydroisophthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are esters of tetrahydroterephthalic acid, among which are monoorganyl esters of tetrahydroterephthalic acid and bisorganyl esters of tetrahydroterephthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl

esters of tetrahydroterephthalic acid and dialkyl esters of tetrahydroterephthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are esters of hexahydrophthalic acid, among which are monoorganyl esters of hexahydrophthalic acid and bisorganyl esters of hexahydrophthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of hexahydrophthalic acid and dialkyl esters of hexahydrophthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. di(2-ethylhexyl) hexahydrophthalate.

Other preferred dust-reduction additives are esters of hexahydroisophthalic acid, among which are monoorganyl esters of hexahydroisophthalic acid and bisorganyl esters of hexahydroisophthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of hexahydroisophthalic acid and dialkyl esters of hexahydroisophthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are esters of hexahydroterephthalic acid, among which are monoorganyl esters of hexahydroterephthalic acid and bisorganyl esters of hexahydroterephthalic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of hexahydroterephthalic acid and dialkyl esters of hexahydroterephthalic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are esters of maleic acid, among which are monoorganyl esters of maleic acid and bisorganyl esters of maleic acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of maleic acid and dialkyl esters of maleic acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}), e.g. di(1-benzyl-2,2,6,6-tetramethylpiperidin-4-yl) maleate.

Other preferred dust-reduction additives are esters of hydroxycarboxylic acids, hydroxydicarboxylic acids, hydroxytricarboxylic acids, hydroxyoligocarboxylic acids,

and/or hydroxypolycarboxylic acids, e.g. tartronic acid, malic acid, tartaric acid, citric acid, etc.

Other preferred dust-reduction additives are esters of citric acid, among which are monoorganyl esters of citric acid and bisorganyl esters of citric acid (examples of organyl being alkyl, oxalkyl, alkenyl, alkynyl, aralkyl, alkylaryl, or aryl), preference being given to monoalkyl esters of citric acid and dialkyl esters of citric acid (alkyl = linear, branched, cyclic, substituted cyclic, or heterocyclic C_1-C_{20}).

Other preferred dust-reduction additives are butyl epoxystearate, hexyl epoxystearate, epoxidized soy oil, epoxidized octyl tallate, epoxidized octyl oleate, tetraethylene glycol di(2-ethylhexoate), and triethyleneglycol di(2-ethylhexoate).

Other preferred dust-reduction additives are esters of mono-, di-, tri-, tetra-, or pentahydric alcohols, and those of higher polyols.

Other preferred dust-reduction additives are mono-, di-, tri-, or tetraorganyl esters of pentaerythritol, and mixtures of these, e.g. pentaerythritol tetrabenzoate.

Other preferred dust-reduction additives are sulfonamide-based compounds, particularly preferably aromatic sulfonamides, e.g. N-ethyltoluenesulfonamide, N-cyclohexyltoluenesulfonamide, N-butylbenzenesulfonamide, N-methylbenzenesulfonamide, N-butylbenzenesulfonamide, p-toluenesulfonamide, N-ethyl-p-toluenesulfonamide, and N-cyclohexyl-p-toluenesulfonamide.

Other preferred dust-reduction additives are glycerol, hexyl glycol, and modified urethane prepolymer which has a weight-average molecular weight of from 400 to 2 000, preferably from 600 to 1 000.

Other preferred dust-reduction additives are esters of p-hydroxybenzoic acid, e.g. hexyloxyethoxyethyl p-hydroxybenzoate, hexyloxypropoxypropyl p-hydroxybenzoate, hexyloxybutoxybutyl p-hydroxybenzoate, octyloxyethoxyethyl p-hydroxybenzoate, octyloxypropoxypropyl p-hydroxybenzoate, octyloxybutoxybutyl p-hydroxybenzoate, 2'-ethylhexyloxyethoxyethyl p-hydroxybenzoate, 2'-ethylhexyloxypropoxypropyl

p-hydroxybenzoate, 2'-ethylhexyloxybutoxybutyl p-hydroxybenzoate, decyloxyethoxyethyl p-hydroxybenzoate, decyloxypropoxypropyl p-hydroxybenzoate, decyloxybutoxybutyl p-hydroxybenzoate.

Other preferred dust-reduction additives are alkyl esters of p-hydroxybenzoic acid, e.g. octyl p-hydroxybenzoate, 2-ethylhexyl p-hydroxybenzoate, heptyl p-hydroxybenzoate, 2-ethyldecyl p-hydroxybenzoate, 2-octyloctyl p-hydroxybenzoate, and 2-decyldodecyl p-hydroxybenzoate.
Other preferred dust-reduction additives are phenols, such as beta-naphthol, dibenzylphenol, and octylcresol.

Phosphorus compounds of oxidation state +5 which may be used are especially alkyl- and aryl-substituted phosphates. Examples are phenyl bisdodecyl phosphate, phenyl ethyl hydrogenphosphate, phenyl bis(3,5,5-trimethylhexyl) phosphate, ethyl diphenyl phosphate, 2-ethylhexyl di(tolyl) phosphate, diphenyl hydrogenphosphate, bis(2-ethylhexyl) p-tolyl phosphate, tritolyl phosphate, bis(2-ethylhexyl) phenyl phosphate, di(nonyl) phenyl phosphate, phenyl methyl hydrogenphosphate, di(dodecyl) p-tolyl phosphate, p-tolyl bis(2,5,5-trimethylhexyl) phosphate, or 2-ethylhexyl diphenyl phosphate. Triphenyl phosphate, and resorcinol bis(diphenyl phosphate) (RDP) and its ring-substituted derivatives are very particularly suitable.

Other preferred dust-reduction additives are tri(butoxyethyl) phosphate, trioctyl phosphate, tricresyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate.

Other preferred dust-reduction additives are organic salts of polyvalent metals, particularly preferably organic salts of elements of the second, third, or fourth main group, or of the second transition group, particularly of the elements magnesium, calcium, strontium, barium, zinc, cadmium, aluminum, tin, lead. Particular preference is given to carboxylic acids having at least 12 carbon atoms, dodecanoic acid (lauric acid), coconut acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid, cetylic acid), octadecanoic acid (stearic acid), cis-9-octadecenoic acid (oleic acid), trans-9-octadecenoic acid (elaidic acid), eicosanoic acid (arachidic acid), docosanoic acid (behenic acid).

The median particle size of the pulverulent flame-retardant composition with low dust level is from 0.1 to 1 000 μm, preferably 1 to 100 μm.

The preferred bulk density of the pulverulent flame-retardant composition with low dust level is from 80 to 800 g/l, particularly preferably from 200 to 700 g/l. Preferred ratios of amounts of dust-reduction additive to those of organophosphorus flame-retardant component are from 1:999 to 1:4, preferably from 1:99 to 1:19.

The invention also provides a process for preparing the inventive pulverulent flame-retardant compositions with low dust level, which comprises emulsifying the dust-reduction additive in water and then adding this emulsion to an aqueous suspension of the organophosphorus flame-retardant component, and stirring at from 20 to 200°C for from 0.1 to 100 hours, removing the solid, washing with water, and then drying.

The detail of this method comprises emulsifying the dust-reduction additive, where appropriate with the aid of a suitable emulsifier (e.g. Arkopal N 090® from the company Clariant GmbH) in water. The aqueous emulsion is added to an aqueous suspension of the OPF, and stirred at from 20 to 200°C for from 0.1 to 100 hours. The solid is then removed. Suitable methods for this are filtering, centrifuging, and decanting. The solid is washed with water. Suitable ratios of solid to washing water are from 1:100 to 1:0.5. The wet solid is then dried at from 20 to 400°C. This may take place in a drying cabinet. However, preference is given to drying in a stream of hot air, e.g. in a spin flash dryer from the company Anhydro, or in a dryer whose operation uses the fluidized-bed principle. Preference is also given to drying at a reduced pressure. Preference is also given to spray-drying of a suspension of the washed solid.

Surprisingly, the inventive dust reduction in an aqueous phase achieves the desired effects at very low contents of dust-reduction additive.

In one embodiment, the inventive pulverulent flame-retardant composition with low dust level may be prepared by adding, in a suitable mixer, the dust-reduction additive in liquid form to the organophosphorus flame-retardant component, which has been

set in motion, and mixing at from 20 to 200°C for from 0.1 to 100 hours, and, where appropriate, then drying at from 20 to 400°C. Dust-reduction additives which are solid at ambient temperature are melted for this process.

In another embodiment, the inventive pulverulent flame-retardant composition with low dust level may be prepared by, in a suitable mixer, adding the solid dust-reduction additive to the organophosphorus flame-retardant component, which has been set in motion, mixing for from 0.1 to 100 hours, and during this process heating to the melting point of the dust-reduction additive. Suitable temperatures are from 20 to 200°C.

Suitable mixers may be: plowshare mixers from the company Lödige, rotating-disc mixers from the company Lödige, (e.g. CB30), Flexomix mixers from the company Schugi, HEC rotating-disc mixers from the company Niro, rotating-disc mixers (e.g. K-TTE4) from the company Drais, Mannheim, Eirich mixers (e.g. R02), Telschig mixers (WPA6), zig-zag mixers from the company Niro.

The product mixture initially produced can be dried in a suitable dryer, or heat-treated to enlarge the particles. Dryers of the invention may be: fluidized-bed dryers from the company Hosokawa Schugi (Schugi Fluid-Bed, Vometec fluidized-bed dryers), fluidized-bed dryers from the company Waldner or from the company Glatt, turbo-fluidized-bed dryers from the company Waldner, spin-flash dryers from the company Anhydro, or else drum dryers.

Preferred operating conditions in the fluidized-bed dryer are: air inlet temperature from 120 to 280°C, product temperature from 20 to 200°C.

The residual moisture level in the inventive pulverulent flame-retardant composition with low dust level is from 0.01 to 10%, preferably from 0.05 to 1%.

The flowability of the inventive pulverulent flame-retardant composition with low dust level, determined by a method based on DIN 53916 and expressed as the cotangent of the angle of repose phi, is preferably from 1 to 2, particularly preferably from 1.2 to 1.8.

The tendency toward dusting of the inventive pulverulent flame-retardant composition with low dust level is from 1 to 65%, preferably from 5 to 60%.

The invention also provides a flame-retardant polymer molding composition which comprises the inventive pulverulent flame-retardant composition with low dust level.

The flame-retardant polymer molding composition preferably comprises
from 1 to 50% by weight of pulverulent flame-retardant composition with low dust level,
from 1 to 99% by weight of thermoplastic polymer or a mixture of the same
from 0 to 60% by weight of additives
from 0 to 60% by weight of filler.

The flame-retardant polymer molding composition particularly preferably comprises
from 5 to 30% by weight of pulverulent flame-retardant composition with low dust level,
from 5 to 90% by weight of the thermoplastic polymer or a mixture of the same
from 5 to 40% by weight of additives
from 5 to 40% by weight of filler.

The flame-retardant polymer molding composition preferably also comprises component B and/or C, as described above.

The thermoplastic polymers are preferably HI (high-impact) polystyrene, polyphenylene ethers, polyamides, polyesters, polycarbonates, or blends or polyblends of the type represented by ABS (acrylonitrile-butadiene-styrene), or PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene).
The thermoplastic polymers are particularly preferably polyamide, polyester, or ABS.

Finally, the invention also provides polymer moldings, polymer films, polymer filaments, or polymer fibers, comprising the inventive pulverulent flame-retardant composition with low dust level.

The polymer of the polymer moldings, polymer films, polymer filaments, or polymer fibers is a thermoplastic or thermoset polymer.

The thermoplastic polymers are preferably HI (high-impact) polystyrene, polyphenylene ethers, polyamides, polyesters, polycarbonates, or blends or polyblends of the type represented by ABS (acrylonitrile-butadiene-styrene), or PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene), polyamide, polyester, and/or ABS.

Preferred thermoplastic polymers are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyacrylonitrile (PAN), and polyacrylates.

The thermoset polymers are preferably formaldehyde polymers, epoxy polymers, melamine polymers, or phenolic resin polymers, and/or polyurethanes.

The polymer moldings, polymer films, polymer filaments, or polymer fibers preferably comprise
from 1 to 50% by weight of pulverulent flame-retardant composition with low dust level,
from 1 to 99% by weight of polymer or a mixture of the same
from 0 to 60% by weight of additives
from 0 to 60% by weight of filler.

The polymer moldings, polymer films, polymer filaments, or polymer fibers particularly preferably comprise
from 5 to 30% by weight of pulverulent flame-retardant composition with low dust level,
from 5 to 90% by weight of the polymer or a mixture of the same
from 5 to 40% by weight of additives
from 5 to 40% by weight of filler.

The inventive pulverulent flame-retardant composition with low dust level is preferably used in compounded materials which are in turn used to produce polymer

moldings. The invention also includes polymer moldings which comprise the inventive pulverulent flame-retardant composition with low dust level.

An example of a method for incorporating the flame-retardant components into thermoplastic polymers consists in premixing all of the constituents in the form of powders and/or granules, in a mixer, and then homogenizing these within the polymer melt in a compounding assembly (e.g. a twin-screw extruder). The melt is usually drawn off in the form of a strand, cooled, and pelletized. The components may also be separately introduced by way of a feed system directly into the compounding assembly.

It is also possible to admix the flame-retardant additions with ready-to-use polymer pellets or with a ready-to-use polymer powder, and to process the mixture directly on an injection molding machine to give moldings.

Preferred fillers are glass (preferably in bead or in fiber form), oxides and/or hydroxides of the elements of the second or third main group of the Periodic Table of the Elements (preferably aluminum and magnesium), phyllosilicates, and clay minerals, e.g. bentonites, montmorillonites, hectorites, saponites, precipitated/fumed/crystalline/amorphous silicas, chalk.

Preferred additives are synergists, antioxidants, light stabilizers, lubricants, colorants, nucleating agents, or antistatic agents. Examples of the additives used are given in EP 0 584 567 A1.

The invention also provides an intumescent flame-retardant coating comprising at least from 1 to 50% of pulverulent flame-retardant composition with low dust level, and from 0 to 60% of ammonium polyphosphate.

Examples

Determination of concentration of dust-reduction additive

50 g of specimen material are weighed into a 500 ml volumetric flask, topped up to the mark with acetone, and stirred on a magnetic stirrer for from 10 to 15 minutes. The mixture is then filtered through a fluted filter (32 cm diameter), and the filtrate is collected in a dry glass vessel. The filtrate, mostly cloudy, is then treated with from 10 to 20 drops of a solution of 10 g of concentrated hydrochloric acid in 100 ml of acetone, and, after thorough mixing, filtered through a double fluted filter (32 cm) into a dry 250 ml volumetric flask. The clear, slightly yellowish filtrate is placed with from 2 to 3 boiling chips in a weighed 500 ml distillation flask. Once most of the acetone has been distilled off, the distillation flask is heated to constant weight at 120°C in an electrically heated drying cabinet. Once the flask has cooled, the amount of additive is determined gravimetrically.

Determination of flowability

Flowability is determined using the PFRENGLE test equipment specified in DIN 53 916. (DIN 53 916 (August 1974 issue): Determination of flowability of powders and granular materials.)

Determination of tendency toward dusting

10 g of the material to be studied are weighed into a wash bottle. Nitrogen is passed through the material for 20 min, using a gas flow rate of 1 l/min. The amount of powder remaining after this procedure is weighed. The proportion discharged is divided by the initial weight, and related to 100%.

Determination of particle size distribution using the Microtrac Granulometer

Particle size in aqueous dispersion is determined with the aid of a Microtrac ASVR/FRA Granulometer from the company Leeds and Northrup. The degree of reflection or scattering of a laser beam is measured as it penetrates the dispersion. For this, 400 ml of ethanol are pumped through the laser measurement cell. The solid specimen (e.g. 70 mg) is metered in automatically, and after 10 min the particle size distribution is determined. The evaluation unit of the equipment calculates the d_{50} value and the d_{90} value.

Preparation, processing, and testing of flame-retardant compounded materials and polymer moldings:

The flame-retardant components are mixed with the polymer granules and, where appropriate, with additives, and incorporated in a twin-screw extruder (Leistritz LSM 30/34) at temperatures of from 230 to 260°C (GR PBT) and, respectively, from 260 to 280°C (GR PA 66). The homogenized polymer strand is drawn off, cooled in the waterbath, and then granulated.

After adequate drying, the molding compositions are processed on an injection molding machine (Aarburg Allrounder) at melt temperatures of from 240 to 270°C (GR PBT) and, respectively, from 260 to 290°C (GR PA 66) to give test specimens.

Example 1 (inventive)

250 g of aluminum diethylphosphinate are dispersed in 1 l of deionized water. The dispersion is heated to 60°C. At the same time, 1 g of Arkopal N 080® and 25 g of di-2-ethylhexyl phthalate (DOP) were weighed out and emulsified with 100 g of deionized water. An amount of the DOP emulsion corresponding to 0.4 g of DOP is added dropwise to the aluminum diethylphosphinate (d_{50} = 49), and the mixture is stirred at 60°C for 1 h. The solid is filtered off, and the filter cake is washed with 1 l of deionized water. The material is dried at 120°C in a vacuum drying cabinet. The product comprises 0.05% by weight of di-2-ethylhexyl phthalate.

Example 2 (inventive)

As in example 1, an amount of the DOP emulsion corresponding to 1 g of DOP is added to the aluminum diethylphosphinate in a dispersion, heated to 60°C, of 250 g of aluminum diethylphosphinate, and the mixture is stirred, the solid is filtered off and washed and dried, and the product obtained comprises 0.12% by weight of di-2-ethylhexyl phthalate.

Example 3 (inventive)

As in example 1, an amount of the DOP emulsion corresponding to 2 g of DOP is added to the aluminum diethylphosphinate in a dispersion, heated to 60°C, of 250 g of aluminum diethylphosphinate, and the mixture is stirred, the solid is filtered off and washed and dried, and the product obtained comprises 0.23% by weight of di-2-ethylhexyl phthalate.

Example 4 (inventive)

As in example 1, an amount of the DOP emulsion corresponding to 10 g of DOP is added to the aluminum diethylphosphinate in a dispersion, heated to 60°C, of 250 g of aluminum diethylphosphinate, and the mixture is stirred, the solid is filtered off and washed and dried, and the product obtained comprises 1.06% by weight of di-2-ethylhexyl phthalate.

Example 5 (inventive)

0.25 g of Genapol 2822® is mixed with 249.75 g of aluminum diethylphosphinate for 5 min in a household multimixer (from the company Braun).

Example 6 (inventive)

2.5 g of Genapol 2822® is mixed with 247.5 g of aluminum diethylphosphinate for 5 min in a household multimixer (from the company Braun).

Example 7 (inventive)

12.5 g of Genapol 2822® is mixed with 237.5 g of aluminum diethylphosphinate for 5 min in a household multimixer (from the company Braun).

Example 8 (inventive)

25 g of Genapol 2822® is mixed with 225 g of aluminum diethylphosphinate for 5 min in a household multimixer (from the company Braun).

Example 9 (inventive)

250 g of Melapur® MP melamine polyphosphate (melamine phosphate) from the company DSM Melapur, NL are mixed for 5 min with 250 g of aluminum diethylphosphinate in a household multimixer (from the company Braun).

Example 10 (inventive)

2.5 g of Genapol 2822 are mixed for 5 min with 247.5 g of the product from example 9 in a household multimixer (from the company Braun).

Example 11 (inventive)

25 parts of the flame retardant from example 10 are mixed with 45 parts of polybutylene terephthalate pellets and 30 parts of glass fibers, and incorporated in a twin-screw extruder (Leistritz LSM 30/34) at temperatures of from 230 to 260°C (GR PBT). The homogenized polymer strand is drawn off, cooled in a water bath, and then pelletized. After sufficient drying, the pellets are processed on an injection molding machine (Aarburg Allrounder) at melt temperatures of from 240 to 270°C (GR PBT) to give moldings. In the UL 94 fire test the V-0 classification is achieved.

Example 12 (inventive)

2 000 g of aluminum diethylphosphinate (d_{50} = 11 µm) are dispersed in about 3 000 g of deionized water. 200 g of Agrocer® 09 are stirred into the dispersed aluminum diethylphosphinate. This mixture is stirred for 1 hour at room temperature. The treated aluminum diethylphosphinate is then filtered off (filter paper: Blauband), and the filter cake is washed with about 3 500 ml of deionized water, and dried at 120°C in a vacuum drying cabinet. This gives 2 020 g of pulverulent flame-retardant composition with low dust level.

Example 13 (inventive)

2 000 g of aluminum diethylphosphinate (d_{50} = 11 µm) are dispersed in about 3 000 g of deionized water. 400 g of Agrocer® 09 are introduced into the dispersed aluminum

diethylphosphinate. This mixture is stirred for 1 hour at room temperature. The treated aluminum diethylphosphinate is then filtered off (filter paper: Blauband), and the filter cake is washed with about 3 500 ml of deionized water, and dried at 120°C in a vacuum drying cabinet. This gives 2 058 g of pulverulent flame-retardant composition with low dust level, with a median particle size d_{50} of 13 μm.

Table

Example	*OPF	Additive		Product				
		Type	Weight used	Additive content	Dusting	Flowability	Bulk density	Median particle size d_{50}
	g		g	%	%	cot phi	g/l	µm
Comp.		-	-	0	66	1.2	677	59
1	250	Di-2-ethylhexyl phthalate (DOP)	0.4	0.05	60	1.4	-	-
2	250	Di-2-ethylhexyl phthalate (DOP)	1	0.12	58	1.4	511	-
3	250	Di-2-ethylhexyl phthalate (DOP)	2	0.23	57	1.5	-	-
4	250	Di-2-ethylhexyl phthalate (DOP)	10	1.06	56	1.7	466	-
5	249.75	Genapol 2822	0.25	0.1	40	-	-	-
6	247.5	Genapol 2822	2.5	1	38	1.6	426	-
7	237.5	Genapol 2822	12.5	5	35	1.3	-	-
8	225	Genapol 2822	25	10	33	1	502	-
10	247.5	Genapol 2822	2.5	1	35	1.5	-	-
12	2 000	Agrocer 09 (23% strength)	200	2.20	27	1.6	389	-
13	2 000	Agrocer 09 (23% strength)	400	4	25	1.5	413	13

*OPF: Organophosphorus flame-retardant component